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[21] International Application Number: PCT/DE97/01118 [22] International Date of Filing: May 30, 1997 [30] Priority dates: 196 22 614.7 June 5, 1996 (DE) 196 34 477.8 August 27, 1996 (DE) [71] Applicant (for all Contracting States, except for the United States): FORSCHUNGSZENTRUM JÜLICH GMBH Wilhelm-Johnen-Strasse D-52425 Jülich, Germany (DE) [74] Joint representative: FORSCHUNGSZENTRUM JÜLICH GMBH Legal and Patent Department D-52425 Jülich, Germany (DE)	[72] Inventors; and [75] Inventors/applicants (only for the United States): ALLGAIER, Jürgen [DE/DE] Alte Vaalser Strasse 10 D-52074 Aachen, Germany (DE) WILLNER, Lutz [DE/DE] Krefelder Strasse 29 D-52070 Aachen, Germany (DE) RICHTER, Dieter [DE/DE] Lankenstrasse 55 D-52428 Jülich, Germany (DE) [81] Contracting States: CA, CN, JP, RU, UA, US, European Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With an international search report. Before expiration of the deadline allowed for amendments to the claims. The publication will be repeated if amendments are made.</i>	
[54] Title: Process for the preparation of hydrophobic-hydrophilic AB block copolymers. [57] Abstract: The invention relates to a process for the preparation of hydrophobic-hydrophilic AB block copolymers wherein block A consists of the monomer unit a, which is conjugated diene, and block B consists of the monomer unit b, which is epoxide, and the invention also relates to the AB block copolymer synthesized by the preparation process, as well as to micellar systems made from the AB block copolymer. According to the invention, the AB block copolymer is synthesized in two steps, whereby the first step is the preparation of block A in a nonpolar solvent and the second step is the preparation of block B in a polar solvent.		

Description

Process for the preparation of hydrophobic-hydrophilic AB block copolymers

The invention relates to a process for the preparation of hydrophobic-hydrophilic AB block copolymers according to Claim 1 as well as to the AB block copolymer synthesized by the preparation process, and to micellar systems made from the AB block copolymer.

According to the state of the art, AB block copolymers are already known in which block A contains monomer units **a**, which are conjugated dienes, such as 1,3-dienes, and block B contains monomer units **b**, which are epoxides. Due to the incompatibility of blocks A and B, such polymers form microphase-separated systems as solids while, in most solvents, they form micellar structures (= opposite solubility behavior of blocks A and B in polar and nonpolar solvents).

Thus, the article by M. Gervais and B. Gallot in *Makromol. Chem. [Macromolecular chemistry]* 178, 1577 (1977) and Dutch patent no. 7,308,061 describe a synthesis of block copolymers having the structure AB and ABA, respectively, whereby A is polybutadiene or polyisoprene and B is polyethylene oxide. In this process, the synthesis takes place in a one-pot reaction by means of the successive addition of diene and of ethylene oxide to form mono-functional or bi-functional organo-sodium or organo-potassium initiators in tetrahydrofuran (THF) as the polar solvent.

German patent no. 23 22 079 describes the synthesis of an AB block copolymer wherein A is polybutadiene and B is polyethylene oxide. Here, too, the synthesis takes place in a one-pot reaction by means of the consecutive addition of the monomers butadiene and epoxide to the initiator *sec*-butyl lithium in benzene. Since this initiator is not

The reaction described in U.S. patent no. 4,254,238 takes place under very aggressive conditions and is consequently very uncontrolled. For example, chains are cleaved. In addition, lithiated tetramethyl ethylene diamine (TMEDA) and unreacted butyl lithium remain in the solution. Among the reaction products, there is also a fraction of homopolyethylene oxide, in other words, a polymer that consists exclusively of epoxide units. However, as is shown in the article titled "Synthesis and properties of uniform polyisoprene networks. I. Synthesis and characterization of α,ω -dihydroxy polyisoprene" in the journal Rubber Chemistry and Technology, volume 49, page 303 (1976), the reaction intermediate products, which only contain two $-\text{CH}_2-\text{CH}_2-\text{O}$ side chains, precipitate out of the solution while forming complex compounds with metal ions. The result is a non-uniform product that contains a high proportion of unreacted components and by-products.

None of the methods cited is capable of yielding an AB block copolymer whose chemical properties are clearly defined in terms of its linearity and chain length and which is free of by-products. In Dutch patent no. 7,308,061, the blocks A, which are comprised of the monomeric diene, have a mixed structure made up of 1-4-polymer and 1-2-polymer or 3-4-polymer.

Therefore, the invention is based on the objective of creating a process for the preparation of AB block copolymers with the monomer units a, which are conjugated diene, and the monomer units b, which are epoxide, a process that yields a product whose structure is clearly defined, whereby the chain lengths of the blocks A and B can be selected at will and can be adjusted by means of the reaction conditions, whereby no branching of the product in the form of side effects occurs and whereby no by-products, such as homopolymers A or B, are formed. Moreover, the blocks A should have a very high proportion of 1,4-polymer. The effort involved for the subsequent purification procedure should be minimal. The process should be inexpensive.

A polymer should be made available whose block A has a low glass transition temperature and an AB block copolymer should be created which, in solvents, can form micellar structures.

On the basis of the generic part of Claim 1, this objective is achieved according to the invention by means of the features indicated in the characterizing part of Claim 1.

With the process according to the invention, it is now possible to prepare an AB block copolymer whose blocks A and B have clearly defined chain lengths, also with respect to each other. The product does not exhibit any branching caused by side chains. Now, molecules can be tailor-made as desired so as to meet the required specifications in terms of chain length, molecular weight, polarity proportion and viscosity. The conversion of the initial materials is quantitative, and a product can be made whose block A contains approximately 95% of 1,4-addition product. Depending on the requirements, it is no longer necessary to add equivalent amounts of sodium or potassium organyl for the polymerization of the epoxide – or of the OH groups – which is brought about as a result of the addition of one unit of epoxide to block A. Nevertheless, homogenous growth is attained.

The subclaims contain advantageous embodiments of the invention.

The preparation process according to the invention for AB block copolymers will be described below.

20 The drawings serve to illustrate the micellar structures made from the AB block copolymers.

The following is shown:

Figure 1: a spherical micellar structure of the AB block copolymer in a solvent (ellipsoidal form also possible);

Figure 2: a cylindrical micellar structure of the AB block copolymer in a solvent;

Figure 3: a lamellar micellar structure of the AB block copolymer in a solvent.

All of the structures depicted in Figures 1 through 3 are possible in nonpolar solvents (in this case, block A is dissolved) as well as in polar solvents (in this case, block B is dissolved).

Table 1 shows the test results cited in the examples.

The following abbreviations are used in the table:

PI	=	OH-terminal-functionalized polyisoprene
PEP	=	OH-terminal-functionalized poly(ethylene propylene)
PEO	=	polyethylene oxide block in the copolymer
^a	=	determined by means of GPC
^b	=	determined by means of NMR from M_n PEP and from the composition
M_n	=	numerical mean molecular weight
M_w	=	weighted average molecular weight
GPC	=	gel-permeation chromatography

The preparation of the AB block copolymer according to the invention takes place in a two-stage synthesis wherein, in the first step, familiar methods are employed to anionically polymerize conjugated diene in a nonpolar solvent using an initiator. A lithium organyl is employed as the initiator. Within the scope of the invention, an AB block copolymer refers to a polymer with at least one block A and at least another block B. In addition to the structure AB, the structure BAB is also a structure according to the invention. In this context, block A consists of a monomer unit **a** or of a mixture of the monomer units **a**, **a'**, **a''**, etc. together. Analogously, block B contains monomer units **b** or a mixture **b**, **b'**, **b''**, etc. Generally speaking, the monomers **a** are conjugated dienes, especially 1,3 dienes. Preference is given to 1,3-dienes which only have short side chains, although, depending on the product desired, it is also possible to employ dienes which either have longer side chains or in which the diene structure is not in a terminal arrangement but rather in a chain. Furthermore, isolated double bonds can also be incorporated into the molecule. Examples are the following compounds: 1,3-butadiene, iso-

prene, 2,3-dimethyl butadiene, 1,3-pentadiene, 1,3-dimethyl butadiene, 2,4-hexadiene. Phenyl groups or their alkyl derivatives can also be in the place of the methyl groups. The decisive factor in the selection of the monomers **a** is that they have to form a nonpolar polymer block A.

The monomer **b** of block B is an epoxide. In the simplest embodiment, the epoxide can be ethylene oxide, although epoxides provided with substituents can also be used in the synthesis. The substituents can be alkyl or aryl substituents.

The decisive factor in the selection of the monomers **b** is that they have to form a polymer block B that is water-soluble. Thus, other monomers that ensure this result can also be employed.

However, when it comes to the monomers **a**, **a'**, **a''** and **b**, **b'**, **b''**, the invention is not limited to the examples cited.

Lithium organyls such as *sec*-butyl lithium or *tert*-butyl lithium can be employed as the initiators for the anionic polymerization of block A. In this context, in view of the solubility of the organyl, preference is given to the use of lithium ion as the counterion. However, a decisive factor is that the organyl ion has to allow the reactive agent to be soluble in the nonpolar solvent that is used in the first reaction step. Over the further course of the reaction, the use of bifunctional lithium organyls, such as a 2:1 adduct from *sec*-butyl lithium and 1,3-*bis*(1-phenyl ethenyl) benzene (MDDPE), leads to AB block copolymers having the structure BAB. The nonpolarity of the solvent allows the reaction course to be controlled in terms of the linearity of the product.

Within the scope of the invention, the term nonpolar solvents refers to a nonpolar aromatic or aliphatic hydrocarbon.

Examples of this are benzene, *c*-hexane, iso-pentane, in other words, branched alkanes as well as alkane.

Once the monomer **a** has been polymerized in the nonpolar solvent by the organyl in order to form a block A, a monomer unit **b** is then grafted onto the still active chain ends. Since lithium initiators are used, no further polymerization occurs. After the reaction is

ended by means of an acid, one obtains the polymer A(OH), which is functionalized with alcoholic OH groups. Subsequently, a familiar method can be employed to hydrogenate A-OH to form the polyolefin A(H)-OH. The terminal OH groups are not attacked by this.

A-OH or A(H)-OH can be precipitated in order to separate lithium salts from the polymer A-OH or A(H)-OH. This has the advantage that Li^+ ions do not interfere with the subsequent reaction.

After the intermediate product A(H)-OH or A-OH has precipitated, it can be isolated and heated up in order to remove impurities. The protic impurities, such as water, alcohols and acids, which are detrimental for the further processing, are removed by repeatedly dissolving the polymers A-OH or A(H)-OH in benzene and by subsequently distilling off or evaporating the benzene under vacuum conditions. Instead of benzene, it is also possible to employ another solvent, such as THF or toluene. In this context, the solvent should dissolve the polymers A-OH or A(H)-OH and remove volatile protic impurities. Due to its high thermal stability, the polyolefin A(H)-OH can be heated to a temperature ranging from 100°C to 120°C [212°F to 248°F] between the individual distillation cycles under vacuum conditions, which increases the effectiveness of the purification process. Depending on the product property, the heating process can also reach higher temperatures such as 150°C to 180°C [302°F to 356°F]. As an alternative, the intermediate product A(H)-OH can be freed of detrimental impurities by means of subsequent heating under vacuum conditions. This eliminates the need to repeatedly dissolve the polymer in the solvent and then having to distill off the solvent.

In the second step, the A-OH or A(H)-OH is dissolved in dry THF or in another polar solvent without allowing contact with air during the procedure, under the reaction conditions commonly employed for anionic polymerization. Examples of other suitable polar solvents are ethers, such as diethyl ether or *tert*-amines. However, the selection of solvents is not restricted to the examples given here.

Potassium-organic or sodium-organic reagents, such as cumyl potassium, are employed to de-protonize the terminal OH groups of the compounds A(H)-OH or A-OH

and to convert them into the macroinitiators A-OK, A-ONa or A(H)-ONa, respectively. Preference, however, is given to potassium compounds. The addition of the epoxide causes grafting of block B and the reaction is subsequently ended with the addition of acid. However, any metal organyl that ensures the solubility of the organyl and of the intermediate reaction products and that allow the polymerization of the epoxide can be employed. Examples of these are benzyl potassium, fluorenyl potassium and naphthyl potassium. Metal hydrides, such as NaH or KH, or else the pure alkali metals, such as sodium or potassium, can be employed as initiators.

As an alternative to the hydrogenation after the first step, the hydrogenation can also follow the polymerization of block B.

The synthesis of the AB block copolymers according to the invention can be carried out under inert gas or in a vacuum, for instance, at 10^{-4} mbar.

Examples

Example 1

Polyisoprene-polyethylene oxide block copolymer: 22.00 grams of isoprene, which had previously been dried for 14 hours at room temperature over solvent-free dibutyl magnesium and then for 20 minutes at -10°C [14°F] over solvent-free n-butyl lithium, are condensed under high-vacuum conditions in a 500-ml glass reactor. Then 300 ml of cyclohexane which had been dried over n-butyl lithium are condensed in addition. Then 1.00 mmol of *sec*-butyl lithium in the form of a solution in cyclohexane is added from an ampoule attached to the reactor. After 24 hours, 0.72 grams of ethylene oxide that has been de-gassed and dried over calcium hydride powder are added via another ampoule. Following an additional 14 hours, the polymerization is stopped by the addition of acetic

acid. The OH-terminal-functionalized polyisoprene is isolated by means of precipitation in methanol.

A total of 8.17 grams of polymer is dissolved in 60 ml of benzene dried over n-butyl lithium. The solvent is distilled off under high-vacuum conditions and the polymer is stirred for 20 hours under high-vacuum conditions. The entire procedure is repeated another two times. Subsequently, without allowing any contact with air, the polymer is dissolved in 60 ml of THF dried over a mixture of sodium-potassium alloy and benzophenone. Under high-vacuum conditions, a 0.05-molar solution of cumyl potassium in THF is added to the polymer solution until the polymer solution acquires a light orange color. Under high-vacuum conditions, 5.89 grams of ethylene oxide that has been degassed and purified over calcium hydride as well as 150 ml of THF are added to the polymer solution. The further polymerization is continued for 3 days at 50°C [122°F] and subsequently ended by the addition of acetic acid. The block copolymer is purified by means of precipitation in cold acetone at a temperature of -20°C [-4°F].

The AB block copolymer forms water-soluble micelles in the order of magnitude of a few microns.

Example 2

Poly(ethylene propylene) polyethylene oxide block copolymer: 7.2 grams of OH-terminal-functionalized polyisoprene from Example 1 are dissolved in 600 ml of heptane and hydrogenated by means of a palladium / barium sulfate catalyst at 90°C [194°F] and at 40 bar of hydrogen pressure. The OH-terminal-functionalized poly(ethylene propylene) obtained is purified by means of precipitation in methanol and dried in a high vacuum at 100°C [212°F] for three days under agitation. The polyethylene oxide block is polymerized as described in Example 1, using 5.51 grams of OH-terminal-functionalized

poly(ethylene propylene) and 2.75 grams of ethylene oxide. The purification of the product is also carried out as described in Example 1.

Example 3

Poly(ethylene propylene) polyethylene oxide block copolymer: OH-terminal-functionalized polyisoprene is prepared as in Example 1, using 29.08 grams of isoprene, 800 ml of benzene, 6.53 mmol of *tert*-butyl lithium and 2.38 grams of ethylene oxide. The polyisoprene is hydrogenated as in Example 2. The reaction of 1.28 grams of OH-terminal-functionalized poly(ethylene propylene) with 4.04 grams of ethylene oxide takes place as in Example 2.

In decane, the AB block copolymer forms micelles.

Example 4

Poly(ethylene propylene) polyethylene oxide block copolymer: 3.64 grams of OH-terminal-functionalized poly(ethylene propylene) are reacted with 1.18 grams of ethylene oxide as in Example 2. The product is purified by means of precipitation in water.

Example 5

Polyisoprene-polyethylene oxide block copolymer: 50 mol-% of the quantity of cumyl potassium that is necessary for a complete de-protonation of the polymeric OH groups is added to 2.14 grams of OH-terminal-functionalized polyisoprene from Example 3 under the same conditions as in Example 1. The number of OH groups is calculated on the basis of the amount and molecular weight of the OH-terminal-functionalized polyisoprene. The

reaction with 6.75 grams of ethylene oxide takes place as in Example 1, except that the reaction time is 7 days.

The block copolymers from Examples 1 through 5 are examined by means of GPC for the presence of polyisoprene-, poly(ethylene propylene)- and polyethylene oxide-homopolymers. No detectable amounts of homopolymer were found in any case (detection limit lower than 1%).

The characterization of the molecular weights of the polymers from Examples 1 through 5 is compiled in Table 1.

Table 1

	M_n (PI or PEP) (osmosis)	M_w/M_n (PI or PEP) (GPC)	M_n (copolymer) (osmosis)	M_w/M_n (copolymer) (GPC)	Composition (NMR)
Example 1	21,500 ^a	1.02	40,400	1.02	41% PEO
Example 2	23,000 ^a	1.02	33,300	1.02	32% PEO
Example 3	4480	1.03	19,200	1.02	75% PEO
Example 4	4480	1.03	5970 ^b	1.04	20% PEO
Example 5	4280	1.03	20,600	1.03	76% PEO

Abbreviations used in Table 1:

PI = OH-terminal-functionalized polyisoprene

PEP = OH-terminal-functionalized poly(ethylene propylene)

PEO = polyethylene oxide block in the copolymer

^a = determined by means of GPC

^b = determined by means of NMR from M_n PEP and from the composition

For the first time, it is now possible to prepare AB block copolymers comprising a polydiene block A and at least one epoxide block B as chemically and molecularly defined materials. By changing the reaction conditions between the polymerization steps 1 and 2, both monomers can be quantitatively polymerized without side reactions. As a result, neither polymeric by-products nor unreacted monomers are found in the product. None of the processes listed in the state of the art is capable of producing these block copolymers without by-products.

Since the quantity ratio of the monomers a and b can be freely selected, varying the block molecular weights of A and B allows a precise adjustment of the properties of the AB block copolymer such as, for instance, its usability as a detergent. This was not possible with the processes known so far.

The use of aliphatic or aromatic hydrocarbons as the solvent for the polymerization of the diene block A allows the latter to be obtained with a maximum proportion of 1,4-microstructure, that is to say, the anionic polymerization is overwhelmingly – up to about 95% – in the form of a 1,4-addition. This translates into a low glass transition temperature for block A, which is desirable or even necessary for the processability, for example, during extrusion as well as for certain applications. The glass transition temperatures achieved are -80°C [-112°F] at 95% 1,4-polymer in the case of 1,3-butadiene polymer, and -70°C [-94°F] at 95% 1,4-polymer in the case of isoprene polymer, in block A. The methods cited in the state of the art, which employ polar solvents, such as THF (tetrahydrofuran), yield polymers with higher glass transition temperatures for block A.

The hydrogenated AB block copolymers are resistant to oxidation and more thermally stable than the products which are only slightly or not at all hydrogenated.

This has a clearly positive impact on the preparation, processing and application. In addition, as long as a hydrogenated polybutadiene having a high proportion of 1,4-polymer was used as the initial product for the second reaction step, the hydrogenated AB block copolymers exhibit a high degree of crystallization and are insoluble in most solvents or else only soluble at high temperatures (for example, in aromatic and aliphatic

solvents). The products according to the invention are soluble in water or in alkanes, depending on the relative chain length of blocks A and B.

The AB block copolymers according to the invention can be employed in the preparation of emulsions and microemulsions. They have blocks A that are soluble in aliphatic alkanes. An exception to this, however, is the hydrogenated 1,3-butadiene having a high fraction of 1,4-polymer.

In solvents and solvent mixtures, the AB block copolymers according to the invention form micellar structures which can be shaped in different ways. The critical micelle concentration (CMC) of the polymeric amphiphiles is smaller than that of low-molecular amphiphiles. As solids, the micellar structures form microphase-separated systems.

The examples given in Figures 1 to 3 are merely a selection of possible micellar structures but these examples should not be construed as a restriction.

The AB block copolymers and micellar systems according to the invention can be employed as emulsifiers in the medical, pharmaceutical and food-product sectors.

Patent Claims

1. Process for the preparation of block copolymers with at least two blocks which consist of various monomers,
characterized in that
the first block is produced in a first reaction step and the second block in a second reaction step.
2. Process for the preparation of hydrophobic-hydrophilic AB block copolymers according to Claim 1, wherein the monomers **a** form a block A that is soluble in nonpolar solvents and the monomers **b** form a block B that is soluble in polar solvents,
characterized in that
block A is produced in a first reaction step in a nonpolar solvent and block B in a second reaction step in a polar solvent.
3. Process for the preparation of hydrophobic-hydrophilic AB block copolymers by means of anionic polymerization according to Claim 1 or 2 wherein the monomer units **a** of block A are a conjugated diene and the monomer units **b** of block B are an epoxide,
characterized in that
block A is produced in a first reaction step in a nonpolar solvent and block B in a second reaction step in a polar solvent.

4. Process according to one of Claims 2 or 3,
characterized in that
block A is polymerized by means of a lithium organyl as the initiator.
5. Process according to one of Claims 2 through 4,
characterized in that
block B is polymerized by means of at least one component of an alkali metal initiator – except for a lithium initiator – from the group of alkali metal organyl, alkali metal hydride and elementary alkali metal as the initiator.
6. Process according to Claim 5,
characterized in that
the lithium initiator in the first reaction step is a bifunctional initiator.
7. Process according to one of Claims 2 through 6,
characterized in that
in order to stop the first reaction step,
 - 1) the epoxide and
 - 2) a proton donor are added.
8. Process according to one of Claims 2 through 7,
characterized in that
the double bonds that occur in block A are at least partially hydrogenated.

9. Process according to Claim 8,
characterized in that
the double bonds are completely hydrogenated.
10. Process according to Claim 8 or 9,
characterized in that
the double bonds that occur in block A are hydrogenated following the addition of
acid.
11. Process according to one of Claims 2 through 10,
characterized in that
after the addition of the proton donor or after the hydrogenation, block A is dis-
solved at least once in a solvent and the solvent is distilled off.
12. Process according to Claim 11,
characterized in that
the solvent is benzene.
13. Process according to Claim 11 or 12,
characterized in that
the distillation is carried out under a vacuum.

14. Process according to one of Claims 11 through 13,
characterized in that
after the distillation, evacuation is carried out at a temperature between room
temperature and 120°C [248°F].
15. Process according to one of Claims 11 through 14,
characterized in that
the distillation is conducted at room temperature.
16. Process according to one of Claims 2 through 10,
characterized in that
after the addition of the proton donor or after the hydrogenation, block A is sepa-
rated out and evacuated.
17. Process according to Claim 16,
characterized in that
evacuation is carried out at a temperature between room temperature and 120°C
[248°F].
18. Process according to one of Claims 2 through 17,
characterized in that
the preparation of block A takes place at a temperature that does not fall below
room temperature.

19. Process according to one of Claims 2 through 18,
characterized in that
the preparation of block B takes place at a temperature between room temperature
and 50°C [122°F].
20. Process according to one of Claims 2 through 19,
characterized in that
block A is made from a pure component a.
21. Process according to one of Claims 2 through 19,
characterized in that
block A is made from at least 2 different monomers a and a'.
22. Process according to Claim 21,
characterized in that
the monomer a is employed at a higher concentration than monomer a'.
23. Process according to one of Claims 2 through 22,
characterized in that
block B is made from a pure monomer b.
24. Process according to one of Claims 2 through 12,
characterized in that

block B is made from at least two components **b** and **b'**.

25. Process according to Claim 24,
characterized in that
the monomer **b** is employed at a higher concentration than monomer **b'**.
26. Process according to one of Claims 2 through 25,
characterized in that
a block A having a chain length of 10 to 2000 monomer units **a** is prepared.
27. Process according to Claim 26,
characterized in that
a block A having a chain length of 20 to 500 monomer units **a** is prepared.
28. Process according to one of Claims 2 through 27,
characterized in that
a block B having a chain length of 10 to 2000 monomer units **b** is prepared.
29. Process according to Claim 28,
characterized in that
a block B having a chain length of 20 to 500 monomer units **b** is prepared.

30. Process according to one of Claims 2 through 29,
characterized in that
AB block copolymers are prepared whose block A has a low glass transition temperature.
31. AB block copolymer,
characterized in that
it was prepared according to one of Claims 1 through 30.
32. Micellar structure,
characterized in that
it consists of an AB block copolymer according to Claim 31.
33. Micellar structure according to Claim 32,
characterized in that
it is contained in a solvent that either does not dissolve block A or does not dissolve block B.
34. Micellar structure according to Claim 32 or 33,
characterized in that
it consists of a mixture of AB block copolymers according to Claim 31.

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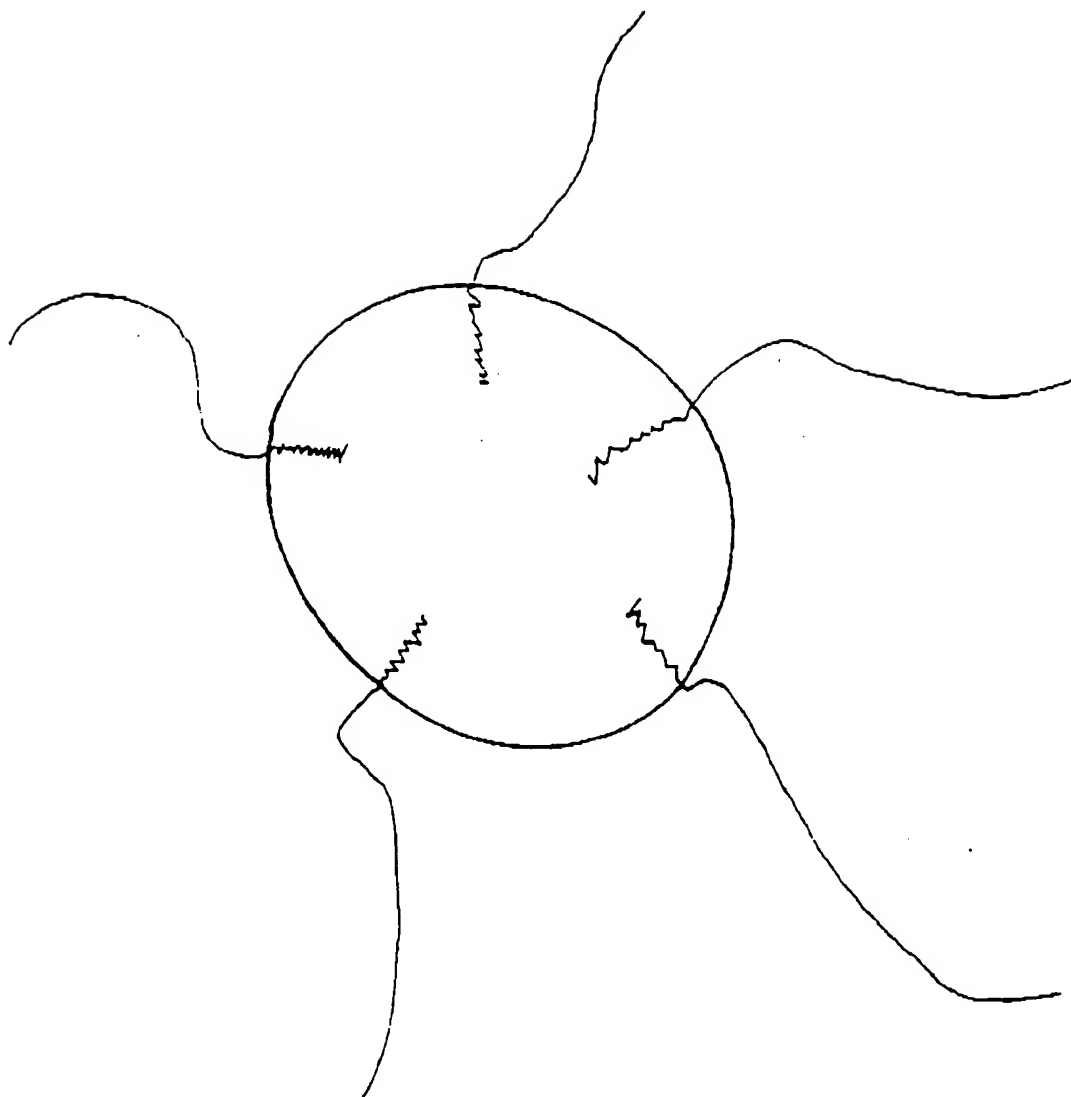


FIG. 1

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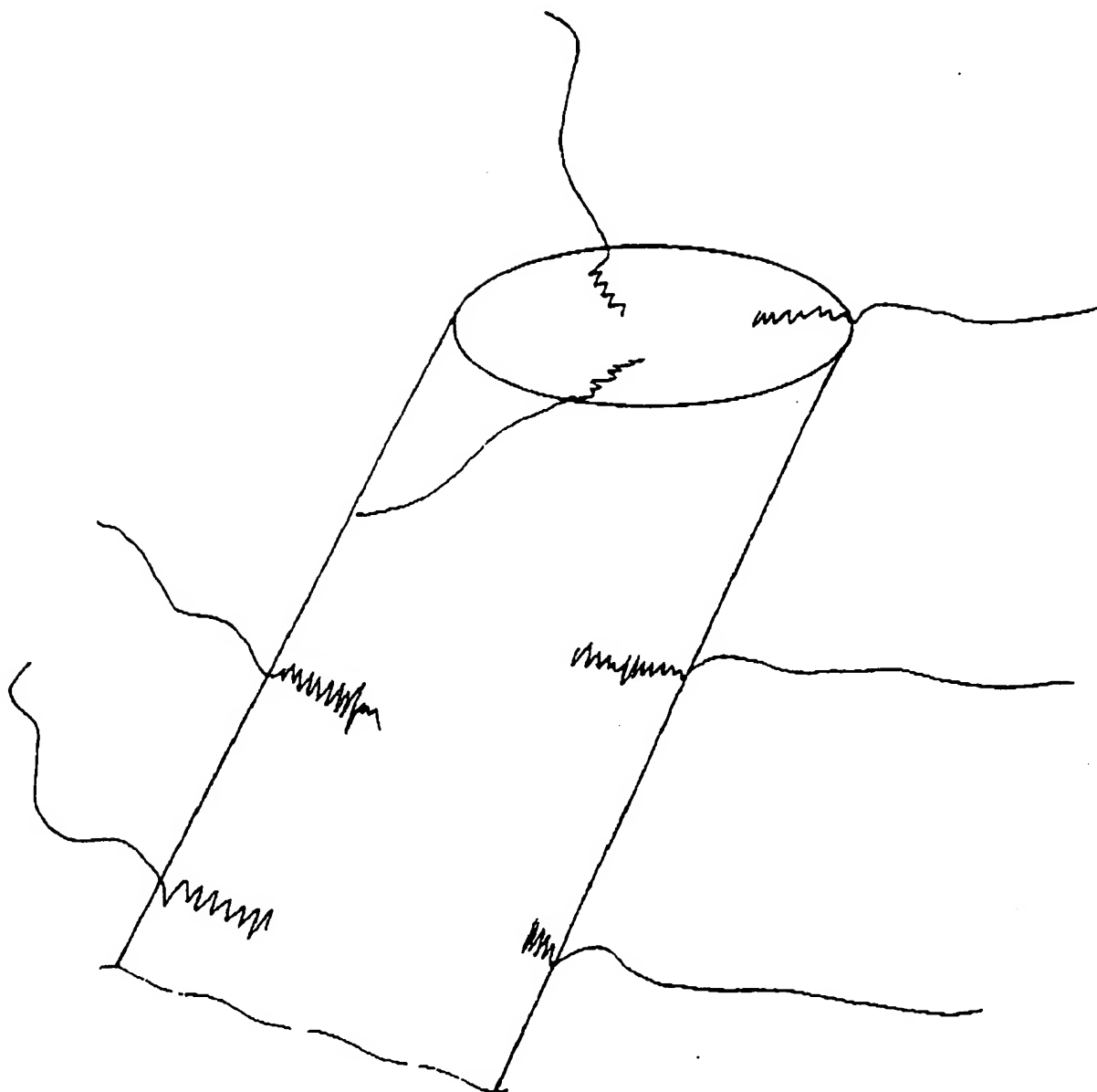


FIG. 2

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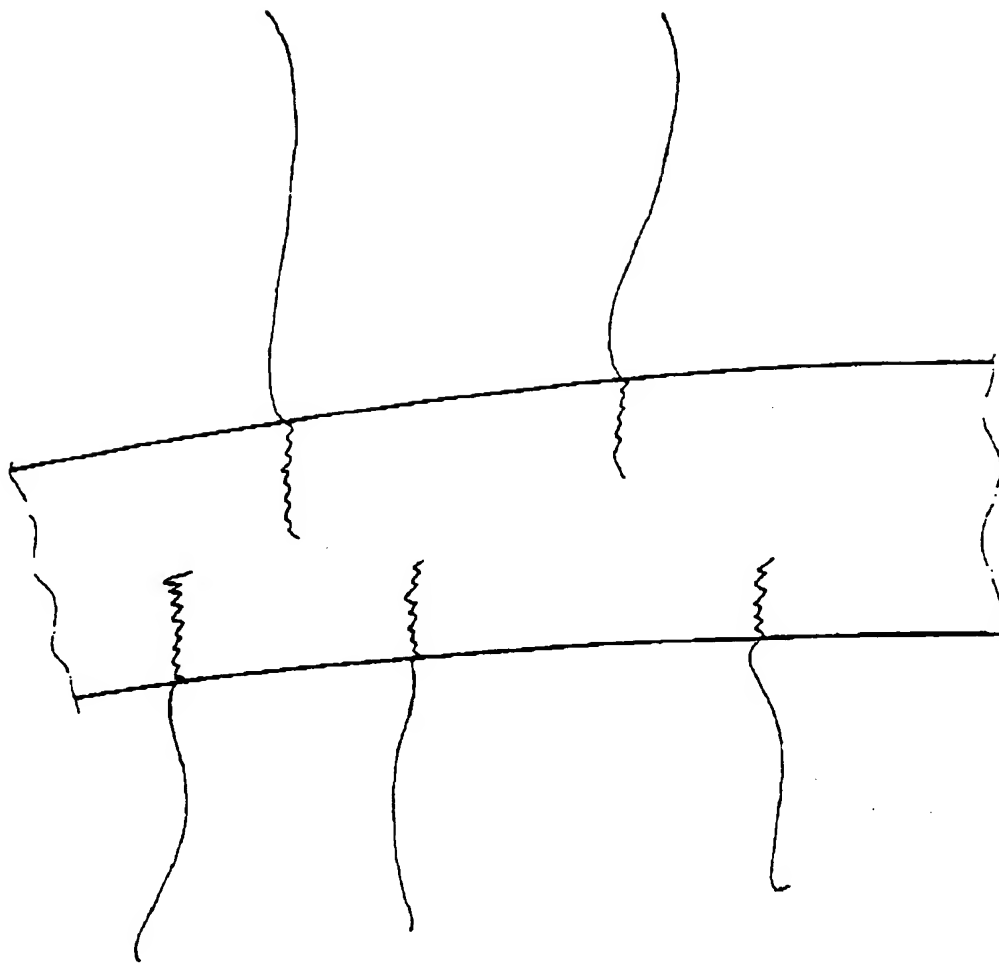


FIG. 3